Chapter 1

Elements of Water Science

1.1 INTRODUCTION

Water is a vital commodity with many remarkable and unique properties. In his elementary textbook on General Chemistry, Pauling (1953) stated: ‘Water is one of the most important of all chemical substances. It is a major constituent of living matter and of the environment in which we live. Its physical properties are strikingly different from those of other substances, in ways that determine the nature of the physical and biological world.’

Water constitutes about 70% of the human body and over 80% of most vegetables. It is the primary biological fluid, being the physicochemical reagent that facilitates the metabolic reactions through which food is converted to energy and new cell material. It is the transport medium that removes waste metabolites from the body and the medium that cools the body through the thermodynamic mechanisms of transpiration, perspiration and respiration.

Water plays an essential role in photosynthesis; this is the process in which water and carbon dioxide are, by the energy of the sun, converted to carbohydrates in green plants, releasing oxygen at the same time. Photosynthesis maintains the level of oxygen in the atmosphere by replacing all that consumed by living organisms; it is also an important provider of dissolved oxygen to rivers and lakes, where it replaces that used up in the biological degradation of organic matter, thus facilitating the process of self-purification.

Because of its remarkable solvent properties and its ability to entrain and transport particulate matter, water is very susceptible to contamination. It is universally used, domestically and industrially, as a transport medium for waste, generating as a consequence large volumes of wastewater.

This textbook outlines the science, technology and engineering of the various processes that are used for the treatment of water to upgrade its quality to meet specific water quality standards. This ‘unit operations’ approach emphasises the common process fundamentals whether used in drinking water production or wastewater treatment systems.

1.2 WATER CHEMISTRY

1.2.1 Structure and composition of water

The experiments of Cavendish and Lavoisier in the 1780s established that water is composed of hydrogen and oxygen in the ratio of two volumes of hydrogen to one volume of oxygen, i.e. the molecular formula for water is H_2O with a molecular weight of 18. Isotopic analysis (Eisenberg and Kaufman, 1969) has indicated, however, that many natural waters contain a very small rare isotope fraction that does not exceed 0.3%.

The water molecule may be described as a ‘bent’ molecule with an atomic configuration, as shown schematically in Fig 1.1. In simple terms, its electronic configuration may be described as consisting of four electron orbitals in which four pairs of outer electrons (six from oxygen and one each from the two hydrogens) are likely to be found. These orbitals are arranged along the directions joining the oxygen atom to the corners of a tetrahedron. Of the four electron orbitals, two are used for the covalent O-H bonds and the remaining two are free orbitals for the remaining so-called lone electron pairs. This electronic configuration confers on the water molecule the important characteristic of charge separation i.e. the resultant centres of positive and negative charge do not coincide. The electrically neutral water molecule can thus be considered as an electric dipole, which would be subject to an orientating moment in an electric field. The moment of the dipole is defined as the product of an electric charge by the distance between the charge centres (units esu.cm). In the gas phase the dipole moment of water is 1.87 x 10^{-18} esu.cm and, owing to molecular association, it becomes somewhat greater in the liquid phase.

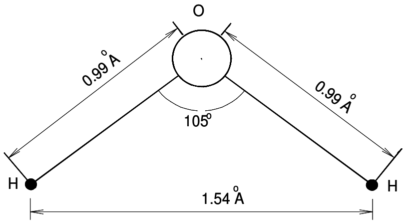

Fig 1.1 **Schematic configuration of the water molecule**

Molecular association, or ‘hydrogen bonding’, which occurs characteristically in ice crystals and is also thought to exist in liquid water, is a further important consequence of the charge separation on the water molecule. Because of this separation the oxygen atom of the water molecule exerts electrostatic attractive forces, in directions corresponding to the orbitals of its lone electron pairs, on the oppositely charged hydrogen atoms of other water molecules. This electrostatic bonding is referred to as hydrogen bonding ad, because of it, the structure of ice is arranged in an ordered lattice framework, in which each oxygen atom is tetrahedrally surrounded by four oxygen atoms. In between any two oxygen atoms is a hydrogen atom which provides the hydrogen bonding. Such a structure of associated water molecules contains interstitial regions which are larger than the dimensions of the water molecule and hence permits the coexistence of free unassociated water molecules.

In liquid water the ordered molecular structure of ice is considered to be partly retained (Pauling, 1960). Its structure may be visualized as consisting of clusters of associated molecules, hydrogen bonded in a tetrahedral framework, plus free unassociated molecules, with continuous interchange between the two. The hydrogen bond is weak relative to the co-valent O-H bond. It has a bond energy of 4.5 kcal $mole^{-1}$ as compared with a value of 110 kcal $mole^{-1}$ for the O-H bond. For this reason, the hydrogen bond is easily broken.

The water molecule dissociates to form hydrogen ions (OH^+) and hydroxyl ions (OH^-). As discussed in subsequent chapters, these ions play a major role in chemical reactions. In combination with the polar nature of the water molecule they are responsible for the remarkable solvent properties of water.

1.2.2 Dissolved substances in water

Substances dissolved in water (solutes) are dispersed in either molecular or ionic form. The concentration of such substances can be expressed in a variety of units, as outlined in table 1.1.

Table 1.1

Basis	Unit
Weight/volume (w/v)	mg l^{-1}, kg m^{-3}
Weight/weight (w/w)	mg kg^{-1}, ppm
Molarity	moles l^{-1}
Molality	moles kg^{-1}
Normality	equivalents l^{-1}

In many water and wastewater treatment situations, the solution density is effectively the same as pure water (in practical engineering computations taken to be 1000 kg m^{-3}; refer table 1.3 for precise values). Hence, the numerical value of the solute concentration, whether expressed as mg l^{-1} of mg kg^{-1}, is effectively the same. By common usage and method of measurement, the w/v form as mg l^{-1} is preferred for waters and wastewaters, while the w/w form is commonly used in practice in relation to concentrated suspensions such as sludges.

The designation of solute concentration in molar units is particularly appropriate for stoichiometric computations relating to aqueous chemical reactions. A one molar solution of a substance contains one mole of the substance per litre of solution, a mole being the mass of a substance equal to its molecular weight in prams, e.g. a mole of oxygen has a mass of 32 grams.

The designation of solute concentration in normality terms is convenient for chemical reactions relating to (1) ion charge, (2) acid-base reactions that involve hydrogen or hydroxyl ion transfer, and (3) oxidation-reduction reactions that that involve electron transfer. A one normal solution of a substance is a solution that contains one 'equivalent weight' of substance per litre of solution. The equivalent weight of a substance is its molecular weight divided by a factor, the value of which is determined by whichever one of the above three chemical environments exists, as illustrated by the following examples:

(1) Ion charge. Iron precipitates from an aqueous solution through the reaction

$$Fe^{3+} + PO_4^{3-} \rightarrow FePO_4(s) \qquad (1.1)$$

The ferric ion has three charges; hence the equivalent weight of iron is its molecular weight/3 = 55.8/3 = 18.6 g. If the iron concentration in solution is 50 mg l^{-1}, then the normality is calculated as follows:

$$\text{normality} = \frac{50\text{x}10^{-3}}{18.6} = 2.69\text{x}10^{-3}\,\text{eq l}^{-1} = 2.69\text{meq l}^{-1}$$

(2) Acid-base reactions. Phosphoric acid dissociates in solution according to the reaction

$$H_3PO_4 \Leftrightarrow 2\,H^+ + HPO_4^{2-} \qquad (1.2)$$

Two hydrogen ions are released and hence the equivalent weight of phosphoric acid is its molecular weight/2 = 98/2 = 49 g. If the concentration of phosphoric acid in solution is 50 mg l^{-1}, then the normality of the solution is calculated as follows:

$$\text{normality} = \frac{50\text{x}10^{-3}}{49} = 1.02\text{x}10^{-3}\,\text{eq l}^{-1} = 1.02\text{ meq l}^{-1}$$

(3) Oxidation-reduction reactions. Ferrous iron is oxidised to ferric iron according to the reaction

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \qquad (1.3)$$

One electron is released and hence the equivalent weight of iron is equal to its molecular weight. If the concentration of iron is 50 mg l^{-1}, then the normality of the solution is calculated as follows:

$$\text{normality} = \frac{50\text{x}10^{-3}}{55.8} = 0.9\text{x}10^{-3}\,\text{eq l}^{-1} = 0.9\text{ meq l}^{-1}$$

1.2.3 Organic matter in water

The concentration of organic matter in water is commonly expressed in terms of the oxygen or equivalent oxygen consumed in its oxidation to carbon dioxide, i.e. in terms of oxygen demand.

The biochemical oxygen demand, of BOD_5, is defined as the oxygen uptake in microbial respiration over a 5-day period during which the water sample is incubated out of contact with light, in a constant temperature environment of 25 ^{o}C. Essentially, BOD is an indirect measure of biodegradable organic matter.

The chemical oxygen demand, or COD, is the oxygen-equivalent of the dichromate consumed in the chemical oxidation of organic matter to carbon dioxide. In the dichromate oxidation-reduction reaction, hexavalent chromium is reduced to trivalent chromium with the loss of three electrons. The equivalent amount of oxygen is computed on the basis that each mole of oxygen accepts four moles of electrons in its reduction to carbon dioxide. COD is an indirect measure of the chemically oxidizable organic matter present in water.

Other measures of organic matter in water that are commonly used in water and wastewater treatment processes discussion are total organic carbon, or TOC, and dissolved organic carbon, or DOC. These are derived from direct instrumental measurements of the amounts of carbon dioxide produced through the oxidation of the organic carbon present in a water sample.

1.2.3 Chemical reactions

Many of the water and wastewater treatment processes discussed in subsequent chapters, are based on the use of chemical reactions to effect a particular change in water quality. Examples include the chemical coagulation process, which is widely used in the production of drinking water to remove colour and turbidity-causing colloidal matter from water; the softening of hard waters to remove calcium and magnesium by chemical precipitation using lime; the removal of heavy metals from wastewaters by chemical precipitation, and many others. In general, the two characteristics of chemical reactions that are of special importance for the process designer are the rate at which reactions take place and the residuals that remain in solution/suspension in the treated water or wastewater. These characteristics are largely determined by the principles of reaction kinetics and chemical equilibrium (Snoeyink & Jenkins, 1980).

Process kinetics is concerned with reaction rates and the environmental factors that influence reaction rates. In general, the rate of chemical reaction is related to the concentrations of the reaction species, which can be stated in mathematical terms as follows:

For the irreversible reaction: $\underset{\text{Reactants}}{A + 2B} \rightarrow \underset{\text{products}}{C + 2D}$

Rate law:

$$\frac{d[A]}{dt} = -k[A]^a[B]^b[C]^c[D]^d \qquad (1.4)$$

Where [ ] indicated molar concentration, k is the reaction rate constant, a, b, c and d are empirical constants.

The value of the rate constant, k is found to increase with increasing temperature according to the semi-empirical Arrhenius relationship:

$$k = Ae^{-(E_a/RT)}$$

where A is a constant for a particular reaction; E_a is the activation energy, which may also be regarded as a constant for a particular reaction; R is the ideal gas constant and T is the absolute temperature (K).

The rate at which some reactions proceed may be greatly accelerated by the presence of a catalyst, which effectively facilitates the reaction without direct participation, i.e. the concentration of the catalyst is not changed by the reaction. Hydrogen ions (H^+) and hydroxyl ions (OH^-) are common catalysts in aquatic systems, as reflected in the extent to which many reactions are influenced by pH. As illustrated in Chapter 17, cobalt ion is used to accelerate the rate of oxidation of sulphite ion (SO_3^{2-}) to sulphate (SO_4^{2-}) by oxygen in the chemical de-oxygenation of water in carrying out oxygenation capacity tests on aeration systems.

As already noted, the residuals that remain in solution following a chemical reaction process are influenced both by the rate of reaction and the solubility of the species involved in the process. The solubility of a substance in water can be defined as its equilibrium concentration in an aqueous solution containing an excess of the substance as a precipitate. The equilibrium state is a dynamic condition in which the forward and reverse rates in a reversible reaction are in balance. Consider the reversible reaction:

$$aA + bB \Leftrightarrow cC + dD$$

rate of forward reaction: $v_f = k_1[A]^a[B]^b$

rate of reverse reaction: $v_r = k_2[C]^c[D]^d$

At equilibrium these reactions are in balance, i.e. $v_f = v_r$ and hence

$$\frac{[C]^c[D]^d}{[A]^a[B]^b} = \frac{k_1}{k_2} = K \qquad (1.8)$$

where K is the equilibrium constant.

Where the reaction is a precipitation reaction, the equilibrium constant is generally called the 'solubility product'. Take, for example, the aqueous equilibrium relationship of the precipitate AB and its dissolved ions:

reaction: $A_aB_{b(s)} \Leftrightarrow aA^{b+} + bB^{a-}$

at equilibrium: $\frac{\left[A^{b+}\right]^a\left[B^{-a}\right]^b}{\left[A_aB_{b(s)}\right]} = K \qquad (1.9)$

By convention the activity of the precipitate is taken to be unity and K is denoted as K_{so} the so-called solubility product. Hence

$$K_{so} = \left[A^{b+}\right]^a\left[B^{a-}\right]^b \qquad (1.10)$$

Solubility product values for a range of precipitates of importance in water and wastewater treatment are given in Table 3.2 in Chapter 3.

One of the key equilibrium relationships in water is its dissociation to form hydrogen and hydroxyl ions:

$$H^+ + OH^- \Leftrightarrow H_2O$$

This reaction proceeds very rapidly so that equilibrium conditions are quickly attained in accordance with the equilibrium condition

$$\left[H^+\right]\left[OH^-\right] = 10^{-14} \qquad (1.11)$$

The hydrogen ion concentration is conventionally expressed in terms of the negative logarithm of its molar concentration or pH. Equilibrium constants are also commonly expressed in pK units.

Another important basic equilibrium relationship that universally applies in aqueous solutions is that of electroneutrality, or charge balance. For example, if the ionic species present are H^+, OH^-, M^{x+} and A^{y-}, then the corresponding charge balance condition is

$$\left[H^+\right] + x\left[M^{x+}\right] = \left[OH^-\right] + y\left[A^{y-}\right] \qquad (1.12)$$

Molar concentration has been the unit of concentration expression used throughout the foregoing discussion of elementary aspects of chemical kinetics and chemical equilibrium. It should be noted, however, that where reactions involve concentrated solutions the molar concentrations have to be modified to take into account the effects of high concentration on reaction rate and reaction equilibrium. In water treatment systems, however, the aqueous solutions are almost invariably dilute.

1.2.5 The carbonate system

The carbonate system plays a key role in the chemical stability of waters, influencing pH, buffer capacity and corrosivity. The component species comprise free gaseous carbon dioxide (CO_2), carbonic acid (H_2CO_3), bicarbonate ions (HCO_3^-) and carbonate ions ($CO_3^=$). Their common element is inorganic carbon and their sum, expressed as molar concentration (or species equivalent) constitutes the dissolved inorganic carbon (DIC) in water

$$DIC = \left[CO_2\right] + \left[H_2CO_3\right] + \left[HCO_3^-\right] + \left[CO_3^{2-}\right] \text{ moles } 1^{-1}$$

Carbon dioxide is taken into solution from the atmosphere; it is also produced in solution by respiring organisms, while it is consumed by photosynthetic organisms. Its equilibrium or saturation concentration in water in contact with atmospheric air is given by the equilibrium relationship:

$$\left[CO_2\right] = K_h P_{CO_2}$$

where $[CO_2]$ is the molar concentration of free carbon dioxide in solution, K_h is the Henry's law constant (see table 1.2), and P_{CO2} is the partial pressure (atm) of carbon dioxide in the atmosphere ($P_{CO2} = 10^{-3.5}$ atm in normal atmospheric air).

The reactions between the carbonate species in water and the related equilibrium constants are as follows:

	Reaction	Equilibrium constant
(a)	$CO_2 + H_2CO_3 \Leftrightarrow H_2CO_3$	Ka
(b)	$H_2CO_3 \Leftrightarrow H^+ + HCO_3^-$	K_b
(c)	$HCO_3^- \Leftrightarrow H^+ + CO_3^{2-}$	K_2

Since only about 0.2% of the free CO2 forms carbonic acid, it is convenient for computation purposes to combine CO_2 and H_2CO_3, denoting their combination as H_2CO_3*:

$$\left[CO_2\right] + \left[H_2CO_3\right] = \left[H_2CO_3^*\right]$$

Reaction (b) is therefore more usually expressed in the form:

$$\text{(d)} \qquad \left[H_2CO_3^{*}\right] \Leftrightarrow H^{+} + HCO_3^{-} \qquad K_l$$

Carbonate is removed from solution through precipitation, most commonly as calcium carbonate:

$$CaCO_{3(s)} \Leftrightarrow Ca^{2+} + CO_s^{2-} \qquad K_{sp}$$

Where the solubility product Ksp = $[Ca^{2+}][CO_3^{2-}]$.

The values of the more commonly used aqueous carbonate system constants in the temperature range 0-60 °C are given in Table 1.2 (it should be noted that $K_l \cong K_a \times K_b$).

Table 1.2 Carbonate system equilibrium constants in pK units

Equilibrium constant	Temperature (°C)						
	5	10	15	20	25	40	60
K_h	1.20	1.27	1.34	1.41	1.47	1.64	1.80
K_l	6.52	6.46	6.42	6.38	6.35	6.30	6.30
K_2	10.56	10.49	10.43	10.38	10.33	10.22	10.14
K_{sp}	8.09	8.15	8.22	8.28	8.34	8,51	8.74

Based on the equilibrium values in Table 1.2, the calculated distribution of the carbonate species in water at 10 °C, as a function of water pH, is plotted in Fig 1.2.

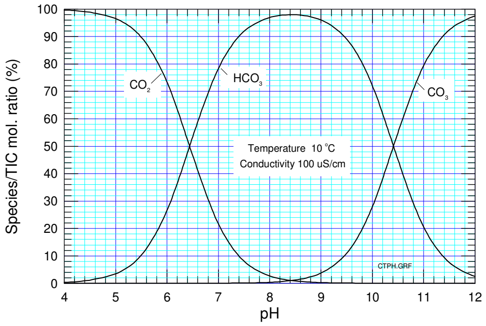

Fig 1.2 **Distribution of carbonate species as function of pH**

The equilibrium concentration of free CO_2 in water in contact with atmospheric air varies from about 1 mg l^{-1} at 0 °C to about 0.5 mg l^{-1} at 20 °C (refer Table 1.9). However, it should be noted that many natural surface waters and groundwaters are found to have CO_2 levels greatly in excess of this value range.

The carbonate system plays a key role in providing natural waters with buffering capacity in respect of pH. Buffering capacity is conventionally expressed in **alkalinity** units, where total alkalinity (T_{alk}) is defined as follows:

$$T_{alk} = \left[HCO_3^{-}\right] + 2\left[CO_3^{-}\right] + \left[OH^{-}\right] - \left[H^{+}\right] \text{ eq l}^{-1}$$

where [ ] indicates molar concentration. It is common practice to express alkalinity as equivalent $CaCO_3$:

$$T_{alk}\ (\text{eq l}^{-1}) \times 50\,000 = T_{alk}\ (\text{mg l}^{-1}\text{ as CaCO}_3)$$

While alkalinity provides a measure of buffering capacity against pH drop on addition of an acid, acidity provides a measure of buffering capacity against pH rise on addition of an alkali. Total acidity (T_{ac}) is defined as follows:

$$T_{ac} = 2[CO_2] + [HCO_3^-] + [H^+] - [OH^-]\ \text{eq l}^{-1}$$

It follows from the definitions of T_{alk} and T_{ac} that:

$$DIC = 0.5(T_{alk} + T_{ac})$$

where T_{alk} and T_{ac} are expressed as eq l^{-1} and DIC is expressed as moles l^{-1}.

1.3 WATER PHYSICS

The physical properties of water, particularly those that influence flow and mixing, have a major bearing on the performance of water and wastewater treatment processes. The properties that influence the flow behaviour of all fluids include density, viscosity and surface tension.

1.3.1 Viscosity

The viscosity of a fluid is the property that defines resistance to flow. It is quantified by the coefficient of dynamic viscosity μ, which is defined by the relationship:

$$\tau = \mu \frac{dv}{dy} \tag{1.13}$$

where t is the shear stress associated with the velocity gradient dv/dy in a flow environment where turbulence is suppressed. The units of dynamic viscosity are N s m^{-2}. The ratio of dynamic viscosity to density (μ/ρ) commonly appears in flow computations; it is known as the kinematic viscosity, has units of m^2s^{-1} and is generally designated by the symbol ν.

The magnitude of the coefficient of dynamic viscosity μ for liquids decreases with increase in temperature. Dynamic viscosity values for water in the temperature range 0-100 °C are given in Table 1.3.

The fluids that exhibit the foregoing behaviour are known as Newtonian fluids. They include waters, wastewaters and gases. The linear correlation of shear stress and velocity gradient, characteristic of Newtonian fluids, prevails only in the absence of turbulence in the flow field. This type of flow is described as *laminar* flow and, for Newtonian fluids, is confined to situations where random bulk fluid movement is suppressed as, e.g. flow in small bore pipes or very close to solid boundaries. Where turbulence exists in the flow, however, the shear resistance is greatly increased and the associated shear stress can, for convenience, be correlated to the velocity gradient by an expression of the same form as that used to define dynamic viscosity:

$$\tau = \varepsilon \frac{dv}{dy}$$

where ε is the coefficient of *eddy viscosity* and is a characteristic of the flow, as distinct from μ which is a property of the fluid. The coefficient of eddy viscosity may be regarded as a coefficient of momentum transfer along the velocity gradient; its magnitude is dependent on the velocity gradient, shear stress, and other factors and is invariably much greater than the dynamic viscosity, μ.

Unlike water and gases, sludges exhibit non-Newtonian behaviour, particularly at high concentration. Non-Newtonian behaviour is characterized by a non-linear relation of shear stress and velocity gradient or rate of shear strain, and, in some fluids, by the existence of a yield stress which must be exceeded for flow to take place (Casey, 1992).

1.3.2 Surface tension

The interfacial liquid at the boundary between a liquid and a gas behaves rather like a membrane which possess tensile strength. This membrane-like behaviour can be quantified as a strain energy per unit area, i.e. Nm m^{-2} of force per unit length (Nm^{-1}), denoted by the symbol σ.

Surface tension causes the capillary rise of water above the phreatic surface in fine-grained saturated soils and porous construction materials. The surface tension influence is generally very small in most fluid flow situations encountered in water and wastewater treatment systems.

The surface tension of water decreases with increase in temperature. It is significantly reduced by surface active agents such as detergents. Surface tension values for water in the temperature range 0-100 ^{o}C are given in Table 1.3.

1.3.3 Vapour pressure

When evaporation takes place from the surface of a liquid within an enclosed space or vessel, the partial pressure created by the vapour molecules is called vapour pressure. A liquid may, at any temperature, be considered to be in equilibrium with its own vapour when the rate of molecular transport through the separating gas-liquid interface is the same in both directions. The absolute pressure corresponding to this concentration of gas molecules is defined as the saturation pressure of the liquid. The saturation vapour pressure of every liquid increases with increase in temperature. The temperature at which it reaches 1 atm absolute is the boiling point, which for water is 100 ^{o}C.

1.3.4 Density

Data on pure water density confirm that water has an open-type structure. Bernal and fowler (1933) estimated that water with a closely packed molecular structure would have a density some 84% greater than the observed value.

Unlike other liquids, water at atmospheric pressure has a negative thermal expansion between 0 ^{o}C and 4 ^{o}C. This anomaly is considered to be related to the competing effects of (a) the breakdown of hydrogen bonding, resulting in a volume reduction, and (b) the increase in the amplitude of molecular vibrations, causing an increase in volume. Between 0 ^{o}C and 4 ^{o}C the volume decrease due to structure breakdown is greater than the volume increase due to increased molecular activity, resulting in a net reduction in volume and corresponding increase in density. Above 4 ^{o}C the vibrational effect is considered to outweigh the structural effect and water density decrease with increase in temperature.

Values of pure water density at atmospheric pressure in the temperature range 0-100 ^{o}C are given in Table 1.3.

Table 1.3 Physical properties of water

Temperature (^{o}C)	Density (kg m^{-3})	Saturation vapour pressure (N m^{-2} x 10^{-3})	Dynamic viscosity (N s m^{-2} x 10^{-3})	Surface tension (N m^{-1} x 10^{3})
0	999.87	0.6107	1.787	75.64
5	999.99	0.8721	1.519	74.92
10	999.73	1.2277	1.307	74.22
15	999.13	1.7049	1.139	73.49
20	998.23	2.3378	1.002	72.75
25	997.07	3.1676	0.890	71.97
30	995.68	4.2433	0.798	71.18
40	992.25	7.3774	0.653	69.56
50	988.07	12.3380	0.547	67.91
60	983.24	19.9240	0.467	66.18
70	977.81	31.1660	0.404	64.40
80	971.83	47.3640	0.355	62.60
90	965.34	70.1120	0.315	60.76
100	958.38	101.3250	0.282	58.90

Source: CRC Handbook of Chemistry and Physics, 67th edn (1987)

While water may be regarded as incompressible in relation to computations involving its density or weight, it is of course an elastic material with a coefficient of compressibility (or bulk modulus) of about 2.1 x 10^{8} Nm^{-2} at 10 ^{o}C. This value increase marginally with increase in temperature and pressure. This property is importance in relation to the transmission of pressure waves through water as, for example, in the so-called 'waterhammer' effect caused by the rapid deceleration of flow in a delivery main following sudden pump trip-out.

The densities of natural waters and wastewaters are greater than pure water at the same temperature. In general, the difference is only of practical significance where the concentration of dissolved or suspended material is high.

The extent by which the densities of aqueous solutions exceed that of pure water is a complex function of salt concentration, temperature and pressure. For practical engineering purposes, the increase in density over pure water (see Table 1.3) may be approximated as follows:

$$\Delta\rho = 0.75\ \mathrm{S} \qquad (1.15)$$

where $\Delta\rho$ is the density increase (kg m^{-3}) over pure water at the same temperature and S is the total salt concentration (kg m^{-3}). Thus the density of brackish water at 10 ^{o}C, having a salt concentration of 4 kg m^{-3}, is 999.73 + 4 x 0.75 = 1002.73 kg m^{-3}.

The density of an aqueous suspension is a function of both the gravimetric concentration of suspended solids and the specific gravity of the solid matter contained in the suspended particles. Consider a suspension of mass M containing p% (w/w) solid matter of dry density ρ_s:

$$\rho_{\text{susp}} = \frac{\text{mass}}{\text{volume}} = \frac{\mathrm{M}}{\left(\frac{\mathrm{p}}{100}\frac{\mathrm{M}}{\rho_{\mathrm{s}}}\right) + \left(\frac{100-\mathrm{p}}{100}\frac{\mathrm{M}}{\rho}\right)}$$

Hence

$$\rho_{\mathrm{susp}} = \frac{\rho}{1 - \frac{\mathrm{p}}{100}\left(1 - \frac{1}{\mathrm{S_g}}\right)} \tag{1.16}$$

where ρ is the density of water and S_g is the specific gravity (ρ_s/ρ) of the dried suspended solids.

1.3.5 Diffusivity

The random movement (Brownian motion) of ions, molecules and very small particles (colloids) in water is known as diffusion. The mean velocity of such species conforms approximately to the basic equation of the simple kinetic theory (Camp and Meserve, 1974):

$$\frac{1}{3}\mathrm{Nmu}^2 = \mathrm{R_u T} \tag{1.17}$$

where N is Avogadro's number (the number of molecules per mole = 6.06 x 10^{23}), m is the mass of each particle (kg), u is the mean velocity of the particles (m s^{-1}), and R_u is the universal gas constant, which has the value 8.3144 J $mole^{-1}$ K^{-1} for a perfect gas, T is the absolute temperature (K). It follows from equation (1.17) that the kinetic energy of solutes and small particles is independent of their size and that their mean velocity is inversely related to the square root of their mass, i.e. the smaller the particle mass the greater is its mean velocity.

The rate of diffusion is defined by the following equation, which is generally known as Fick's law (Crank, 1956):

$$\frac{\partial m}{\partial t} = -D\frac{\partial c}{\partial x} \tag{1.18}$$

where ∂m/∂t is the rate of mass transfer per unit area in the x-direction, ∂c/∂x is the concentration gradient of the diffusing species in the x-direction, and D is the diffusion coefficient or diffusivity, the magnitude of which defines the mass diffusion rate. The units of D are $length^2/time$, usually expressed as $cm^2 s^{-1}$. Some aqueous diffusion coefficient values are presented in Table 1.4.

Table 1.4 Diffusion coefficients in pure water

Solute	Molal concentration	Temperature (°C)	Diffusivity, D (cm^2 s^{-1})
Oxygen (O_2)	-	20	2.03 x 10^{-5}
Nitrogen (N_2)	-	20	1.88 x 10^{-5}
Carbon dioxide (CO_2)			
Hydrochloric acid (HCl)	0.1	19	2.56 x 10^{-5}
Sulphuric acid (H_2SO_4)	1.0	12	1.30 x 10^{-5}
Sodium chloride	0.1	15	1.09 x 10^{-5}
Calcium chloride ($CaCl_2$)	2.0	10	0.79 x 10^{-5}
Chlorine (Cl_2)	0.1	12	1.41 x 10^{-5}
Ammonia (NH3, NH_4^+)	1.0	15	1.78 x 10^{-5}

Source: Camp and Meserve (1974)

It is important to note that diffusion is the dominant transport mechanism only where turbulent bulk water movement is suppressed. This is rarely the case in water and wastewater treatment systems. Thus, for example, while the rate of oxygen transfer from air into surface waters is largely controlled by a diffusion process in the interfacial water film, its transport into the water body is much more rapid, so much so that the oxygen concentration variation in the bulk water phase is generally negligible.

1.3.6 Water-dispersed particles

Water-dispersed species range in size from *true solutes*, i.e. ions and molecules to suspended particles visible to the naked eye. Fig 1.3 categorizes the more significant water-dispersed species by size range.

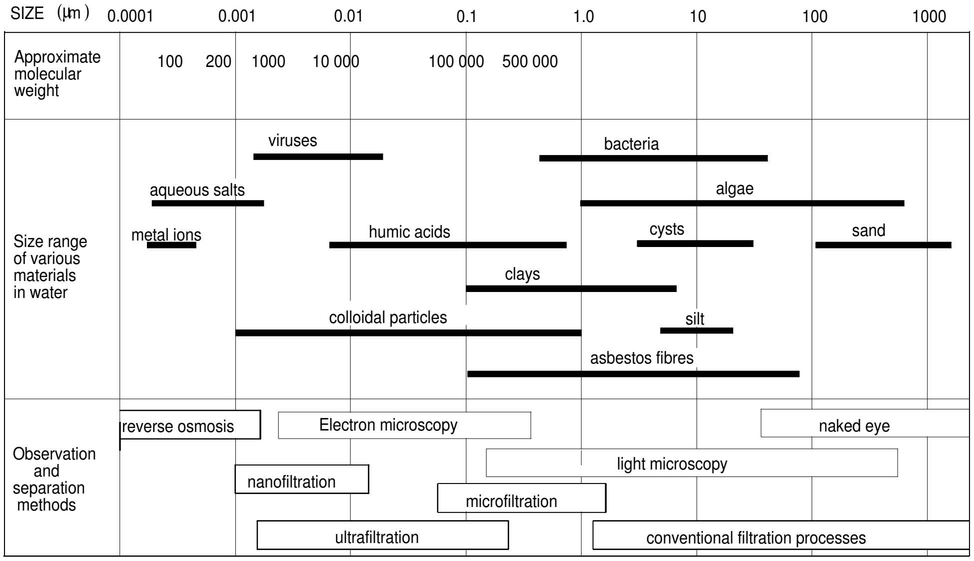

Fig 1.3 **Characteristics of water-dispersed species**

Ions and inorganic molecules may be regarded as true solutes, ranging in size up to about 10^{-3} µm. Low molecular weight organic molecules such as glucose (MW = 180) also belong in this category. High molecular weight organics such as proteins and polymers are an order of magnitude larger and fall within the size range 10^{-3} to 10^{-2} µm.

Dispersed particles that are smaller than about 1 µm and larger than true solutes are designated as *colloids* and exhibit characteristic colloidal properties. As indicated in Fig 1.3, they can be observed only by means of an ultra microscope or an electron microscope. Although colloids are too small to be observed by the naked eye, when viewed at right angles to a light beam, colloidal outlines can be distinguished (Tyndall effect). As briefly discussed in section 1.3.5, colloidal particles are subject to Brownian motion, having a mean velocity that conforms approximately to equation (1.17). It follows from this equation that the average kinetic energy of colloidal particles ($0.5\ mu^2$) is independent of their size. Thus, the mean velocity of the smallest colloidal particle (10^{-3} µm) is calculated from equation (1.15) to be about 100 ms^{-1}, while the velocity of the largest colloidal particle (1 µm) is calculated to be only about 0.004 ms^{-1}. Colloidal dispersions have a high degree of stability and are not amenable to removal by sedimentation or conventional sand filtration processes. The nature of colloidal stability and the processes used to bring about colloidal destabilisation are discussed in Chapter 3. The uniform kinetic energy of colloidal particles, resulting in the very small colloidal particles having very high mean velocities, is a critical factor in the destabilization process.

There is no direct method of measuring the concentration of colloidal particles in water. Turbidity measurement, however, provides a useful index of colloid concentration. Turbidity or cloudiness in water results from the light-scattering effect of very small particles, the outline of which is not visible to the naked eye. It is measured (APHA Standard Methods, 1992) by reference to a standard aqueous turbidity range produced by the dispersion of formazin in water of zero turbidity. Turbidity is normally expressed in nephelometric turbidity units (NTU).

The dispersed species, categorized as *total suspended solids* (TSS), may be loosely regarded as those solids greater in size than colloids. The TSS concentration is measured by filtration through glass-fibre filter paper having a pore size in the range 1-1.6 μm, the retained residue being dried to a constant weight at a temperature of 103-105 ^{o}C.

The 'fixed' suspended solids concentration is the residue remaining after the dried TSS residue is ignited to constant weight at a temperature of 550±50^{o}C. The loss on ignition at this temperature represents the volatile suspended solids.

Settleable solids constitute a subset of TSS, being the fraction which is separated to form a visibly defined settled solids residue after settling for 1 hour. The settleable solids concentration may be expressed in volumetric (ml l^{-1}) or gravimetric (mg l^{-1}) units. The volumetric measurement of settleable solids is made using an Imhoff cone in which a 1 litre sample is allowed to settle under quiescent conditions foe a period of 1 hour.; the settleable solids concentration in volumetric terms is represented by the volume occupied by the settled solids at the base of the cone. The gravimetric concentration is determined as the difference between the measured TSS of a test sample and the TSS remaining in the supernatant after a 1 hour period of quiescent settling.

Living organisms also constitute an important category of dispersed matter in waters and wastewaters. While the larger algae and protozoa are of a size that can be observed by the naked eye (see Fig 1.2), most microorganisms, with the exception of viruses, can be observed using a light microscope and can be separated from water by membrane filtration techniques. Viruses, however, are an order of magnitude smaller that the smallest bacteria. They can be observed only under the magnification of the electron microscope and require membrane filters in the ultrafiltration range for their separation from waters and wastewaters.

1.4 GAS-WATER INTERACTIONS

A number of the unit treatment processes used in water and wastewater treatment systems involve a gas phase. These processes include aeration, dissolved air flotation, disinfection, anaerobic digestion and decarbonation. The gases of relevance include oxygen, ozone, nitrogen, carbon dioxide, air, methane, hydrogen sulphide, ammonia, chlorine and sulphur dioxide.

1.4.1 Gas properties

The thermodynamic properties of a gas govern the interrelation of pressure, volume and temperature, which for most gases is defined by the equation of state for the so-called perfect gas, usually written in its general form as follows:

$$PV = mR_u\theta \tag{1.19}$$

where P is the absolute pressure (N m^{-2}), V is the gas volume (m^3), m is the mass of gas (mole), R_u is the universal gas constant (J $mole^{-1}$ K^{-1}), and θ is the absolute temperature (K). The perfect gas has an R_u value of 8.3144 J $mole^{-1}$ k^{-1}.

Changing from mole to kg, equation (1.19) may be written for individual gases in the form:

$$\frac{P}{\rho} = R\theta \qquad (1.20)$$

where ρ is the gas density (kg m^{-3}) and R is the specific gas constant (J kg^{-1} K^{-1}), related to R_u as follows:

$$R = \frac{1000R_u}{w} \qquad (1.21)$$

where w is the molecular weight.

The constant R can be shown to be the difference between the specific heat capacity of a gas at constant pressure (C_p) and its specific heat capacity at constant volume (C_v). Values for these thermodynamic properties are given in Table 1.5.

The relationships embodied in equations (1.19) and (1.20) may also be expressed in the forms:

$$PV^{\gamma} = \text{constant} \qquad (1.22)$$

or

$$\frac{P}{\rho^{\gamma}} = \text{constant} \qquad (1.23)$$

where V is the gas volume (m^3) and γ is the so-called polytropic exponent. The value of γ depends on the process by which the gas undergoes volume change. For adiabatic processes (zero internal energy loss), γ is equal to the specific heat ratio C_p/C_v, whereas for isothermal processes (zero temperature change), γ is equal to unity. Thus, in real situations, the value of γ lies within the range 1.0 to Cp/Cv.

Gases are relatively highly compressible, their compressibility depending on temperature and pressure. The coefficient of compressibility K for a gas is given by the relation:

$$K = P\gamma \qquad (1.24)$$

Table 1.5 Thermodynamic properties of gases

Gas	Cp (J kg^{-1} K^{-1})	C_p/C_v	R (J kg^{-1} K^{-1})
Air	1005.0	1.40	287.1
Oxygen	929.0	1.40	262.9
Nitrogen	1040.0	1.40	297.1
methane	2260.0	1.31	534.8
Carbon dioxide	867.0	1.30	202.2

Values relate to 25 °C and 1 atm; K = °C + 273.15

Source: CRC Handbook of Tables for Applied Engineering Science, 2nd. edn (1976)

Thus, the coefficient of compressibility, which is a measure of the stiffness of a gas, increases with pressure, which means that gases become less compressible with increasing pressure.

The dynamic viscosity of gases increases with temperature according to the following empirical correlation (Maitland and Smith, 1972):

$$\ln\left(\frac{\mu}{S}\right) = A\ \ln\theta + \frac{B}{\theta} + \frac{C}{\theta^2} + D \tag{1.25}$$

where μ is the dynamic viscosity (N s m^{-2}) at temperature θ (K); S is the dynamic viscosity (N s m^{-2}) at a standard temperature of 293.2 K; and A, B, C and D are coefficients determined from a least-squares regression analysis. Recommended values for these coefficients are presented in Table 1.6.

Table 1.6 Dynamic viscosity coefficients for gases

Gas	A	B	C	D	S (N s m^{-2}x10^7)
Air	0.63404	-45.6380	380.87	-3.4500	182.0
Oxygen	0.52662	-97.5893	2650.70	-2.6892	203.2
Nitrogen	0.60097	-57.0050	1029.10	-3.2322	175.7
Methane	0.54188	-127.5700	4700.80	-2.6952	109.3
Carbon dioxide	0.44037	-288.4000	19312.00	-1.7418	146.7

Source: Maitland and Smith (1972)

1.4.2 Gas solubility in water

With respect to their solubility, the gases of interest in water and wastewater treatment can be split into two categories: (a) the poorly soluble gases which include oxygen (O_2), ozone (O_3), nitrogen (N_2) and methane (CH_4), and (b) gases of medium to high solubility including carbon dioxide (CO_2), ammonia (NH_3), hydrogen sulphide (H_2S), sulphur dioxide (SO_2), chlorine (Cl_2) and chlorine dioxide (ClO_2).

The poorly soluble gases, namely oxygen, ozone, methane and nitrogen conform to Henry's law which states that the solubility of a gas in a liquid with which it is in contact is proportional to the partial pressure of the gas in the gas phase:

$$c_s = H_m p \tag{1.26}$$

where c_s is the equilibrium or saturation concentration (moles l^{-1}) of the gas in solution, p is the partial pressure (atm) of the gas in the gas phase in contact with the liquid and H_m is the Henry law constant. Thus H_m represents the gas solubility at a partial pressure of 1 atm. It is more convenient for general engineering use, however, to express gas solubility in w/v or w/w units at a gas pressure of 1 atm, inclusive of the aqueous vapour pressure, as presented in Tables 1.7-1.9, inclusive. Data for the low solubility gases are presented in Table 1.7 in units of mg l^{-1}, while data for the higher solubility gases are presented in Table 1.8 as % by weight or g per 100 g. The solubility values for these latter gases, which react with water, include all chemical species of the gas in solution. Solubility data for the atmospheric gases at an air pressure of 1 atm, inclusive of the aqueous vapour pressure, are presented in Table 1.9.

Table 1.7 Solubility of low solubility gases in water in mg l^{-1} at a pressure of 1 atm, inclusive of the aqueous vapour pressure

Gas	Temperature (°C)										
	0	5	10	15	20	25	30	35	40	45	50
Oxygen (O_2)	69.9	60.9	53.8	48.1	43.4	39.4	36.1	33.2	30.8	28.5	26.5
Ozone (O_3)	41.4	35.8	29.8	24.1	18.9	13.7	9.6	6.6	4.3	2.7	1.6
Methane (CH_4)	39.8	34.4	30.0	26.4	23.7	21.5	19.9	18.3	17.1	16.1	15.4
Nitrogen (N_2)*	29.4	26.0	23.1	20.8	19.0	17.5	16.2	15.0	13.9	13.0	12.2

Source: CRC handbook of Chemistry and Physics (1961, 1992); Horvath (1975)

*98.81% N2 by volume + 1.185% by volume A

Table 1.8 Solubility of high solubility gases in water as **% by weight** at a pressure of 1 atm, inclusive of the aqueous vapour pressure

Gas	Temperature (°C)						
	0	5	10	15	20	25	30
Carbon dioxide (CO_2)	0.3346	0.2774	0.2318	0.1970	0.1688	0.1449	0.1257
Chlorine (Cl_2)	-	1.160	0.990	0.850	0.730	0.640	0.567
Chlorine dioxide (ClO_2)	19.08	15.38	12.46	10.12	8.25	6.74	5.52
Ammonia (NH_3)	98.0	81.0	69.5	60.0	51.7	45.2	40.4
Hydrogen sulphide (H_2S)	0.7066	0.6001	0.5112	0.4411	0.3846	0.3375	0.2983
Sulphur dioxide (SO_2)	22.83	19.31	16.21	13.54	11.28	9.41	7.80

Source: Handbook of Chemistry and Physics (1961, 1992); Horvath (1985)

Table 1.9 Solubility of atmospheric gases in water (mg l^{-1}) at an air pressure of 1 atm, inclusive of the aqueous vapour pressure

Gas	Temperature (°C)										
	0	5	10	15	20	25	30	35	40	45	50
O_2	14.64	12.76	11.27	10.08	9.08	8.25	7.57	6.95	6.45	5.97	5.61
N_2*	23.25	20.66	18.52	16.76	15.30	14.08	13.05	12.16	11.38	10.67	10.01
CO_2	1.00	0.83	0.70	0.59	0.51	0.43	0.37	0.33	0.29	0.26	0.17
Air**	38.89	34.25	30.49	27.43	24.89	22.76	20.99	19.44	18.12	16.90	15.79

*Nitrogen + Argon

**Air volume fractions: 0.7810 N_2, 0.2095 O_2, 0.0092 A, 0.0003 CO_2

REFERENCES

American Public Health Association (1992) *Standard Methods for the Examination of Waters and Wastewaters*, 18th edn, APHA/AWWA/WEF, Washington, USA.

Bernal & Fowler (1933) V. *Chem. Phys.*, 1, 515.

Camp, T. R. and Meserve, R. L. (1974) *Water and its impurities*, 2nd edn, Dowden, Hutchinson & Ross Inc., PA, USA.

Casey, T. J. (1992) *Water and Wastewater Engineering Hydraulics*, Oxford University Press, Oxford, UK.

Crank, J. (1956) *The Mathematics of Diffusion*, Clarendon Press, Oxford, UK.

CRC Handbook of Tables for Applied Engineering Science, 2nd edn (1976), CRC Press Inc., Boca Raton, Florida, USA.

CRC Handbook of Chemistry and Physics, 73rd edn (1992/93), CRC Press Inc., Boca Raton, Florida, USA.

Eisenberg, D. and Kaufman, W. (1969) *The Structure and Properties of Water*, Oxford University Press, Oxford, UK.

Horvath, A. L. (1975) *Physical Properties of Inorganic Compounds*, Edward Arnold Ltd., London, UK.

Maitland, G. C. and Smith, E. B. (1972) *J. Chem. Eng. Data*, 17, No. 2, 150-155.

Pauling, L. (1960) *General Chemistry*, 2nd edn, W. H. Freeman & Co., San Francisco, USA.

Snoeyink V. L. and Jenkins, D. (1980) *Water Chemistry*, John Wiley & sons, New York, USA.

Related reading

Franks, F. ed. (1971-82) *Water. A Comprehensive Treatise*, 7 Vols, Plenum Press, New York.